

## Benzobisoxazole cruciforms: A tunable, cross-conjugated platform for the generation of blue OLED materials

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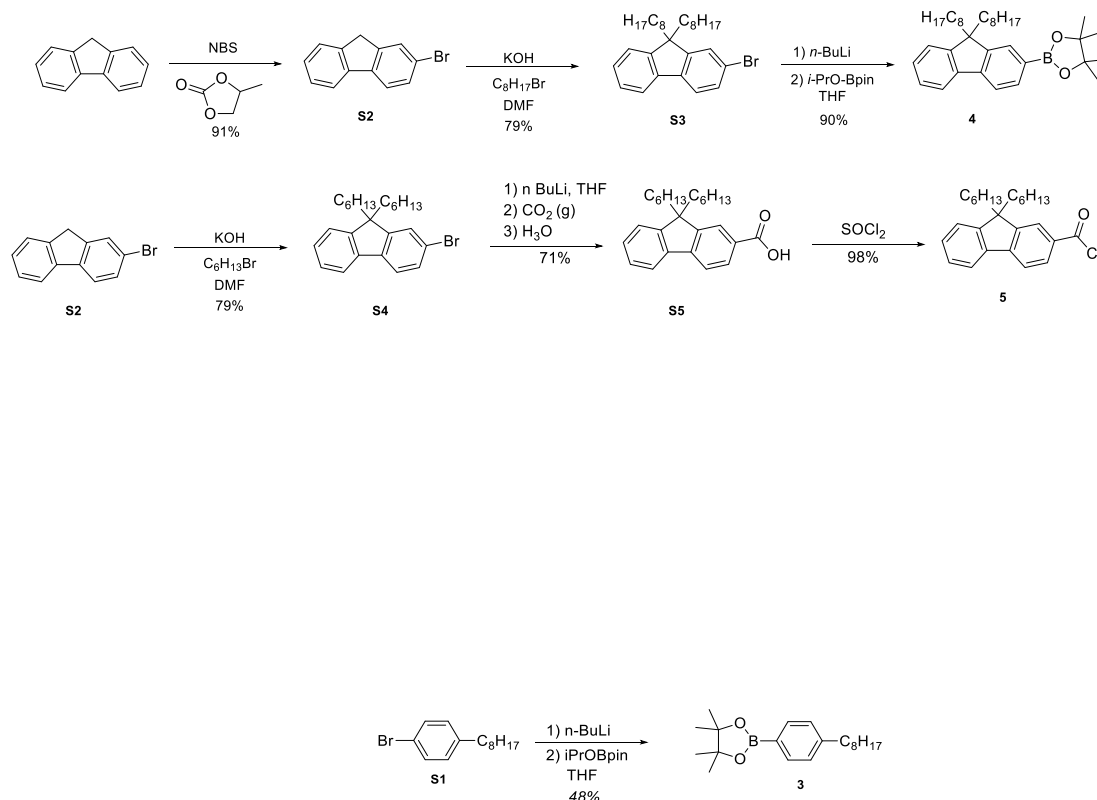
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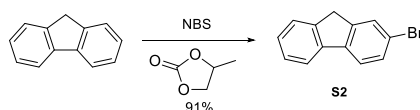
## SYNTHESIS:



### Scheme S1. Synthesis of 4,4,5,5-tetramethyl-2-(4-octylphenyl)-1,3,2-dioxaborolane

In a oven-dried RBF with a stirbar, 4-octylbromobenzene (1.34 g, 5 mmol) was dissolved in dry THF and cooled down to -78 °C by acetone/dry ice bath. Then *n*-BuLi (2.4 mL, 6 mmol) was added dropwise and allowed to stir for one hour. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.22 mL, 6 mmol) was added dropwise and allowed to warm to room temperature overnight. One milliliter of 1M HCl was added to quench the reaction stirred for one hour. 50 mL of water was added to the reaction mixture and then extracted with diethyl ether (3x50 mL). The combined organic layers was washed with brine and dried with sodium sulfate. The solution was filtered and reduced in vacuo. The crude yellow oil was purified by column chromatography (gradient hexanes to 80/20: hex/EtOAc) to resulting in a viscous colorless oil. 48 %

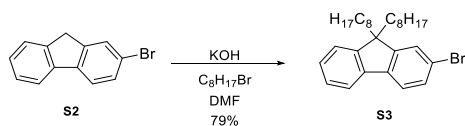
<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) 7.72 (2H, d), 7.19 (2H, d), 2.61 (2H, t), 1.61 (2H, t), 1.34 (2H, s), 1.29 (3H, m), 1.26 (6H, dd), 0.87 (4H, t)



### <sup>1</sup>Scheme S2. Synthesis of 2-bromo-9H-fluorene (S2)

A 250 mL RBF was charged with a stir bar, fluorene (7.45g, 44.8 mmol) and propylene carbonate (56 mL). The solution was heated to 60 °C while stirring vigorously resulting in a yellow solution. The *N*-bromosuccinimide (8.77 g, 49.28 mmol) was added in one portion to give an orange-red color and the solution was immediately allowed to cool to room temperature. The reaction mixture was then poured into chilled water (500 mL) and the slightly pink precipitate was filtered and washed with cold ethanol. The crude product was then recrystallized with an ethanol/water mixture (75:25) which resulted in a white powder and collected from two crops of the same filtrate. 91%

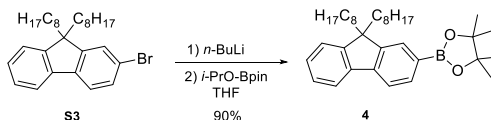
<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) 7.76 (1H, d) 7.68 (1H, s), 7.64 (1H, d), 7.54 (1H, d), 7.51 (1H, d), 7.38 (1H, t), 7.33 (1H, t), 3.89 (2H, s)



### <sup>2</sup>Scheme S3: Synthesis of 2-bromo-9,9-dioctyl-9H-fluorene

With a modified literature procedure...in a RBF under argon, 2-bromofluorene (20 mMol) was dissolved into DMF (40 mL). Tetrabutylammonium bromide (0.84 g, 2.64mmol) was added in as a phase-transfer catalyst. Powdered KOH (4.98 g, 88 mMol) was added in one portion, followed by the dropwise addition of 1-bromooctane (8.11g, 42 mmol). The solution was allowed to stir over night and then poured in 400 mL water. The solution was poured into water and washed with DCM (3x100 mL). The combined organic layers were washed with brine and dried with sodium sulfate and concentrated in vacuo. The crude yellow oil was purified by a hexanes column and basic alumina plug to result as colorless oil. 79%

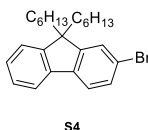
<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) 7.66 (1H, m), 7.55 (1H, d), 7.45 (2H, d), 7.32 (3H, m), 1.93 (5H, ddd), 1.28 (8H, m), 0.89 (9H, t), 0.59 (5H, m)



### **<sup>3</sup>Scheme 4: Synthesis of 2-(9,9-dioctyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**

2-bromo-9,9-dioctyl-9H-fluorene (4.53g, 9.65 mmol) was dissolved in dry THF (50 mL) and chilled to -78 °C. To the solution *n*-BuLi (5.8 mL, 14.5 mmol, 2.5M in hexanes) was added dropwise and allowed to stir for 1 hour. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.94 mL, 19.3 mmol) was added dropwise over 5 minutes and the solution was allowed to warm over room temperature and stirred overnight. The reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with 1M HCl, water, brine then dried with sodium sulfate. The solution was filtered and solvent was removed *in vacuo* and product was purified via column chromatography (gradient hexanes to 50/50 hex/EtOAc) to afford a viscous colorless oil. (92%)

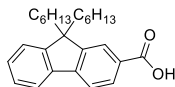
<sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>) 7.80 (1H, d), 7.74 (1H, s), 7.71 (1H, dd), 7.69 (1H, d), 7.32 (3H, m), 1.97 (4H, dtd), 1.39 (12H, s), 1.19 (4H, q), 1.05 (16H, m), 0.81 (6H, t), 0.58 (4H, m)



### **Scheme S4: Synthesis of 2-bromo-9,9-dihexyl-9H-fluorene**

The dihexyl fluorene was prepared similarly as S3. The crude yellow oil was purified by a hexanes column and basic alumina plug to result as colorless oil. 79%

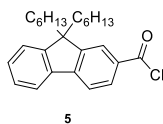
<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>) 7.66 (1H, m), 7.55 (1H, m), 7.46 (2H, m) 7.32 (3H, d), 1.93 (5H, dt), 1.06 (11H, m) 0.78 (5H, m), 0.60 (4H, d)



#### Scheme S5: Synthesis of 9,9-dihexyl-9H-fluorene-2-carboxylic acid

In a dry, 2-necked RBF under argon, dihexyl fluorene (8.03 g, 20 mmol) was dissolved in dry THF (100 mL) and cooled -78 °C. The *n*-BuLi (10 mL, 25 mmol) and was allowed to stir for 90 minutes. Carbon dioxide was bubbled through the solution and allowed to warm to room temperature overnight. The reaction was quenched with 6M HCl and extracted with ether. The combined organic layers were washed with 1M HCl, water, brine and dried over sodium sulfate. Solution was filtered and concentrated in vacuo. The crude oil was purified by column chromatography (hexanes: ethyl acetate 99:1 then gradient to 75:25 after first spot eluted) to result in a viscous yellow oil. 71%

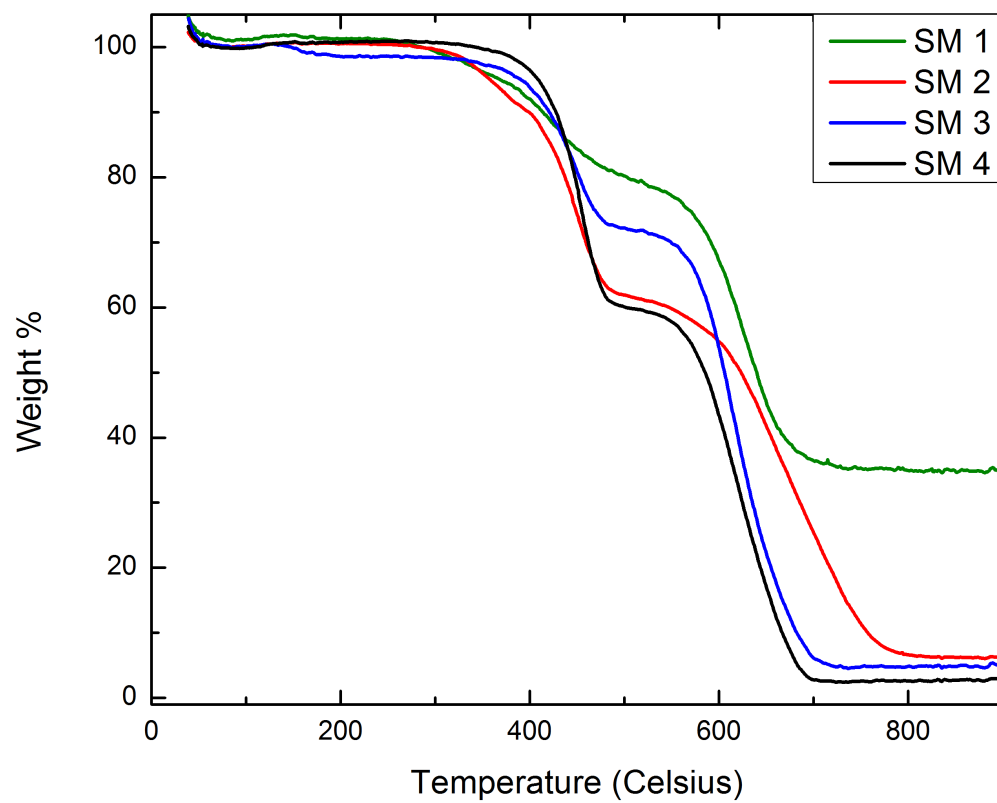
<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>) 8.15 (1H, dd), 8.10 (1H,s), 7.80 (2H, d), 7.38 (3H, m), 2.02 (4H, m), 1.06 (12H, m), 0.76 (6H, t), 0.59 (4H, m)



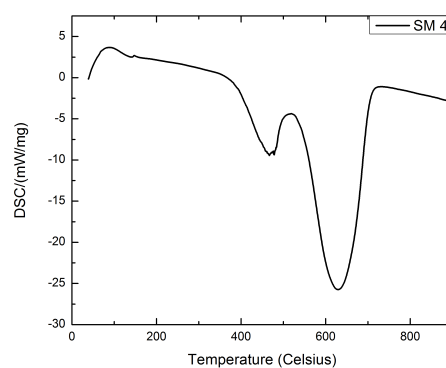
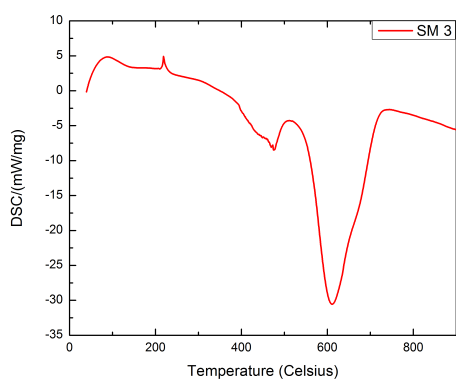
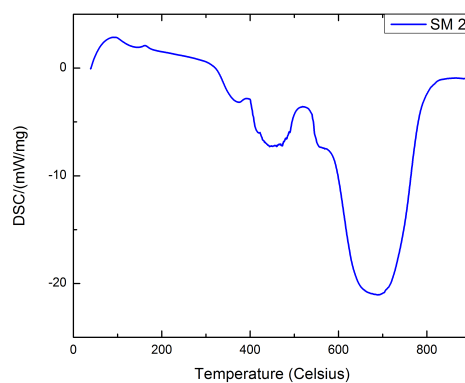
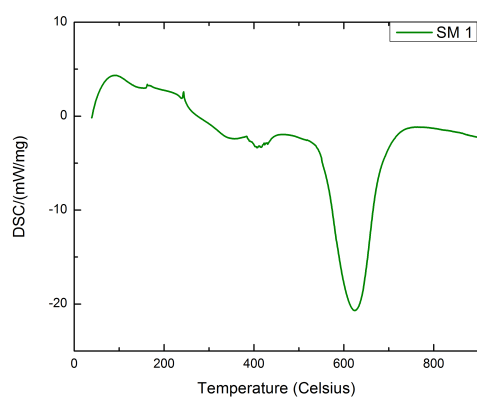
#### Scheme 5: Synthesis of 9,9-dihexyl-9H-fluorene-2-carbonyl chloride

In dried 100 mL RBF, S5 (5.40 g, 14.26 mmol) SOCl<sub>2</sub> (14 mL) and 1 drop of DMF were added and headed to reflux. The excess SOCl<sub>2</sub> was distilled under reduced pressure followed by a subsequent distillation by with 25 mL to remove excess volatiles and was used without further purification resulting in yellow goo. 98 %

<sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>) 8.16 (1H, dd), 8.05 (1H, s), 7.79 (2H, d), 7.40 (3H, m) 2.01 (4H, m), 1.06 (13H, m), 0.76 (6H, t), 0.57 (4H, td)

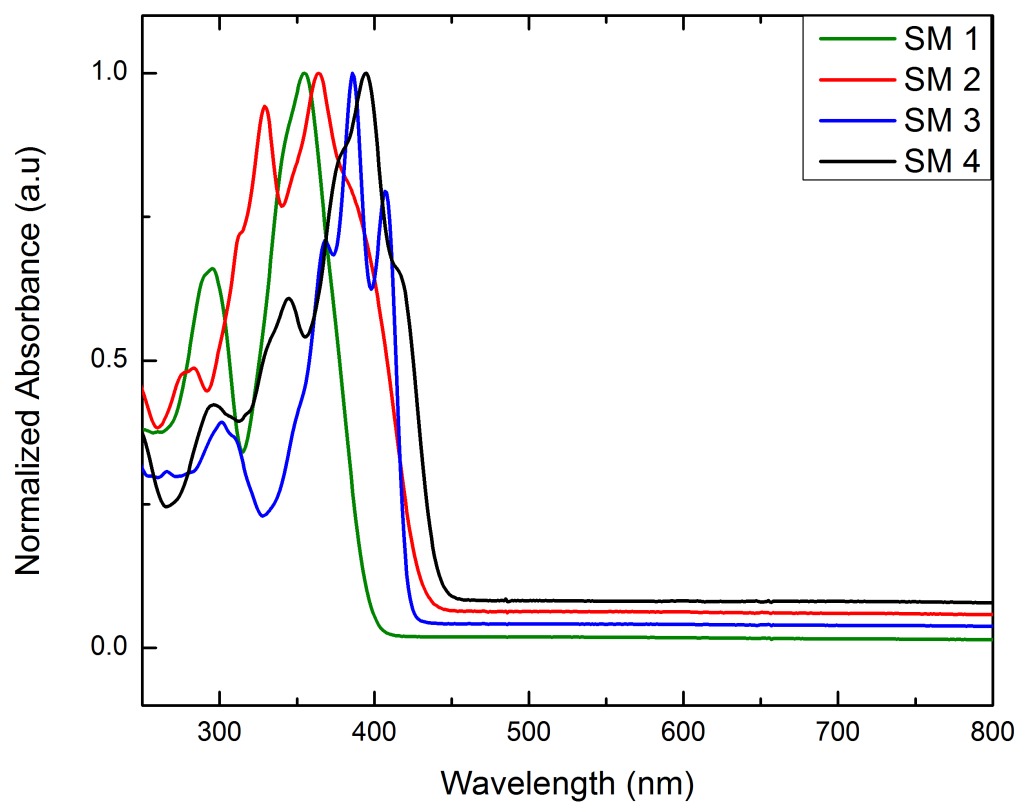


**Figure S2: Thermal gravimetric analysis of Small Molecules 1-4 under air at 20 °C per minute.**

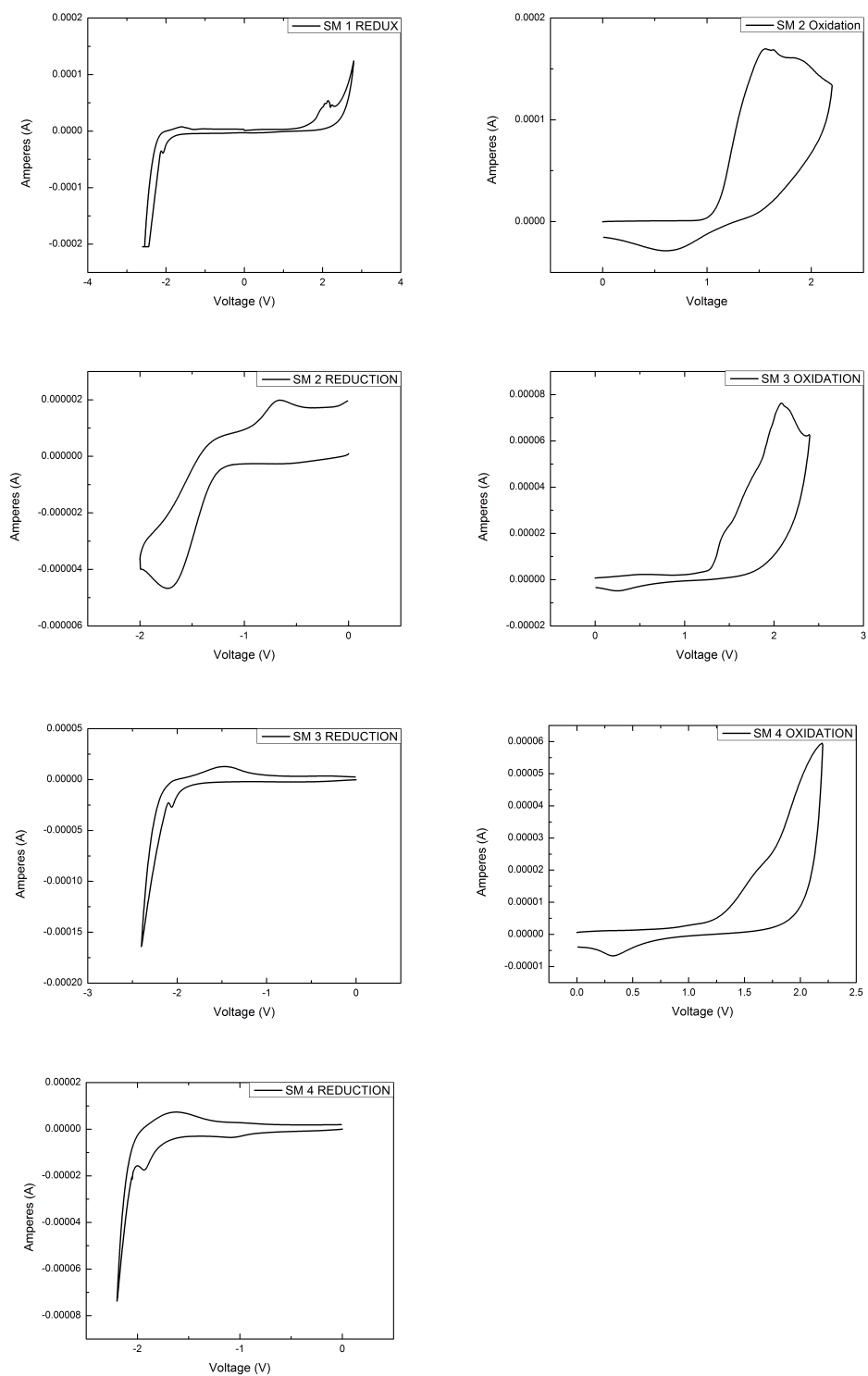


**FIGURE S3: Differential scanning calorimetry for Small Molecules 1-4 under air at 20 °C per minute.**

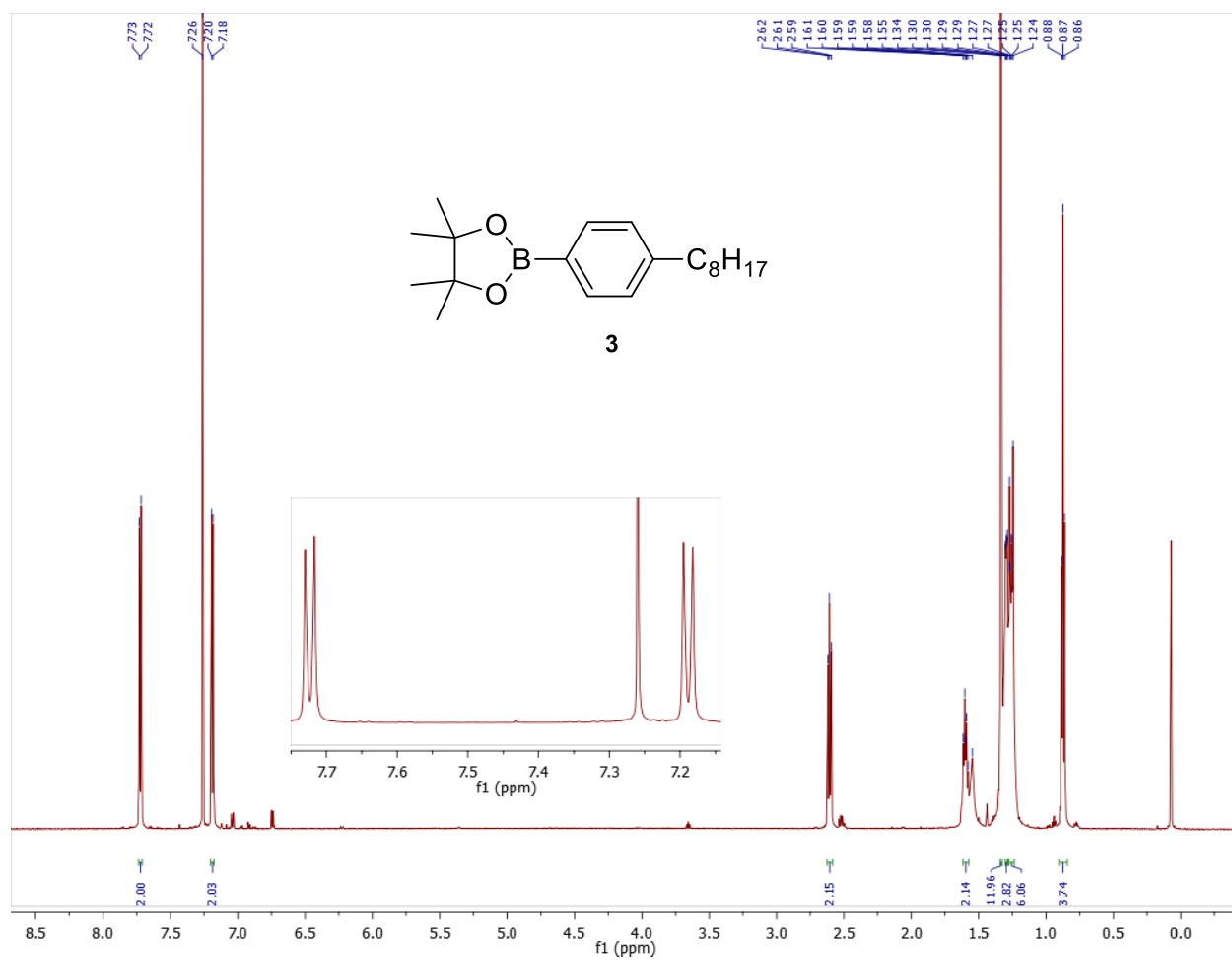




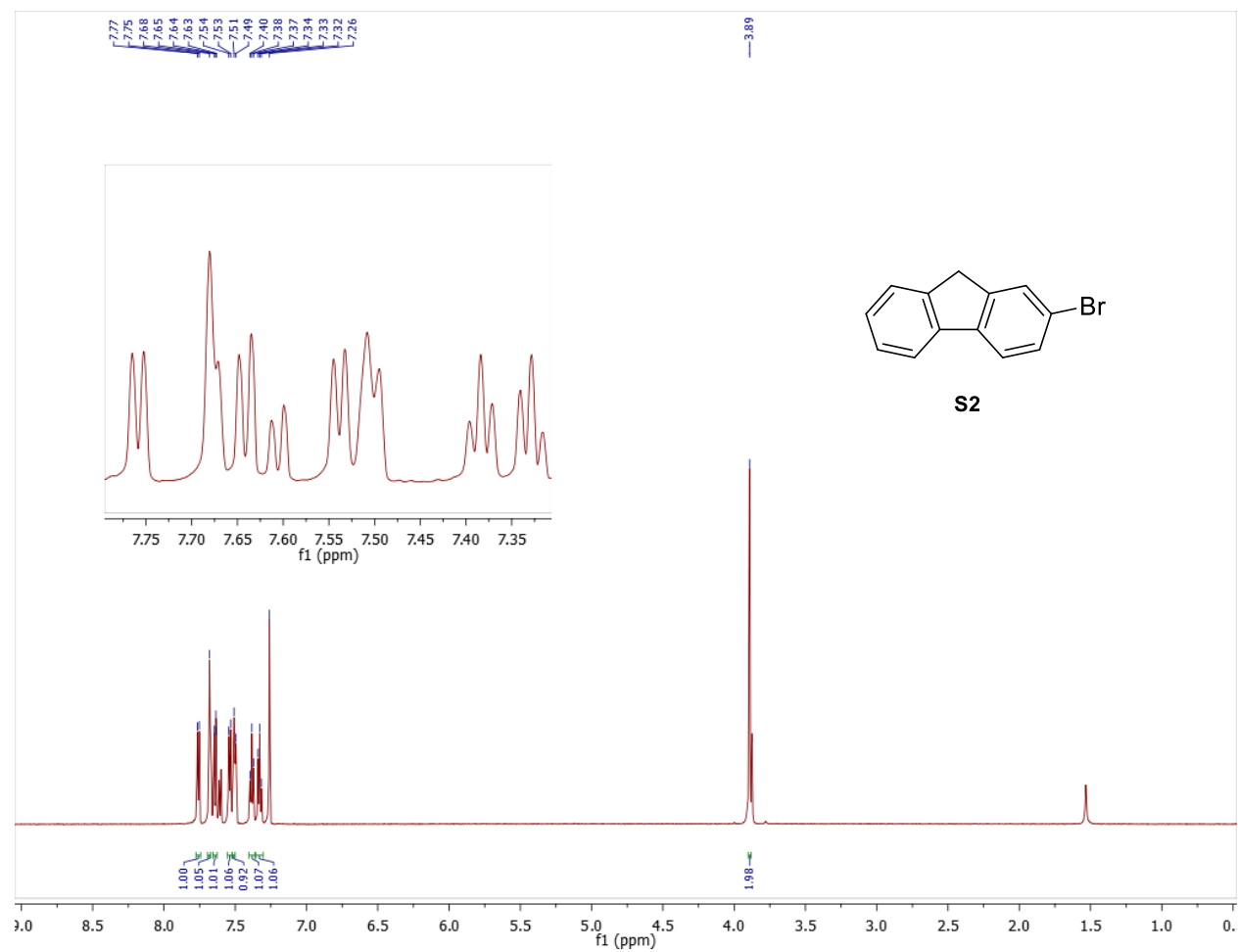
**FIGURE S4: UV-VIS for Small Molecules 1-4**



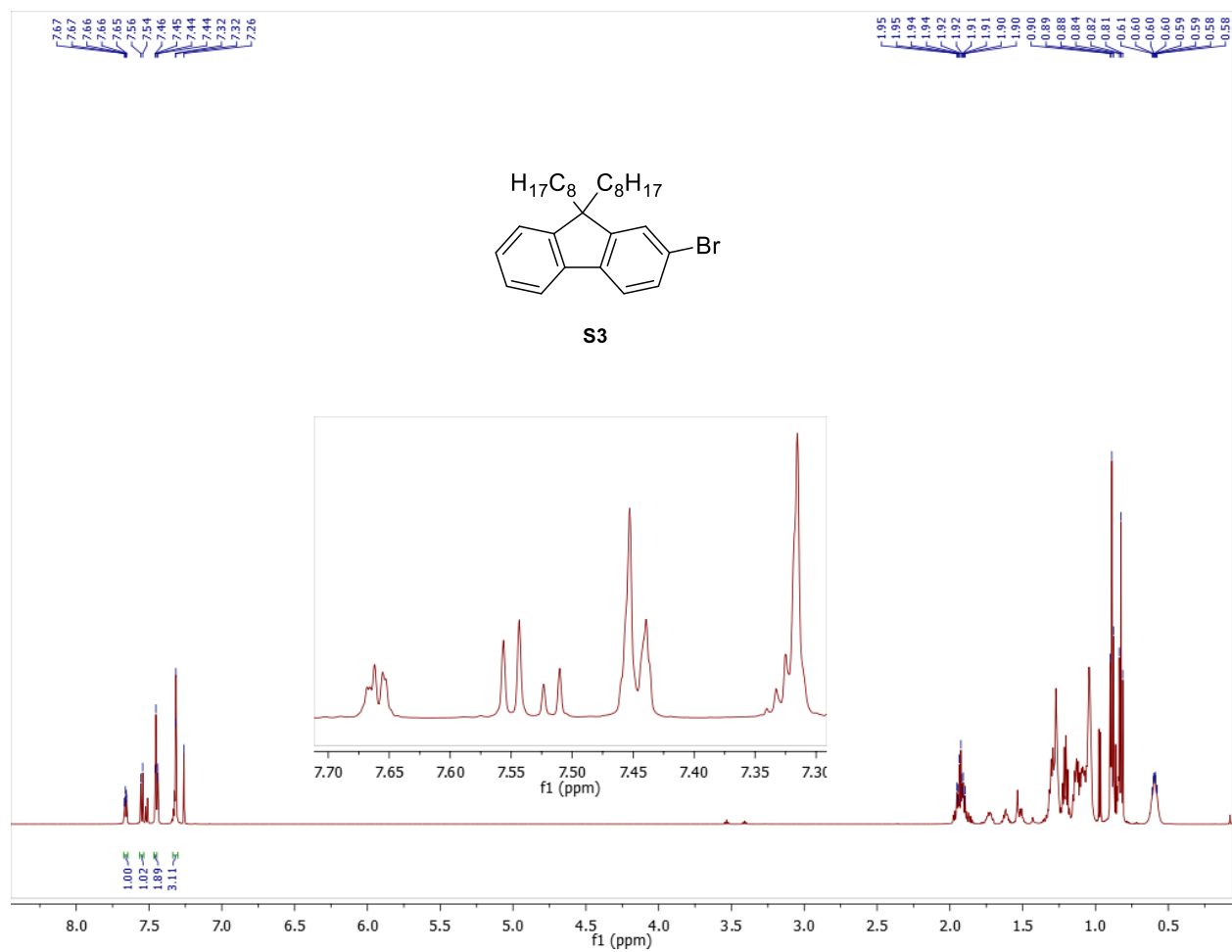
**Figure S5: Cyclic voltammograms of small molecules 1-4**



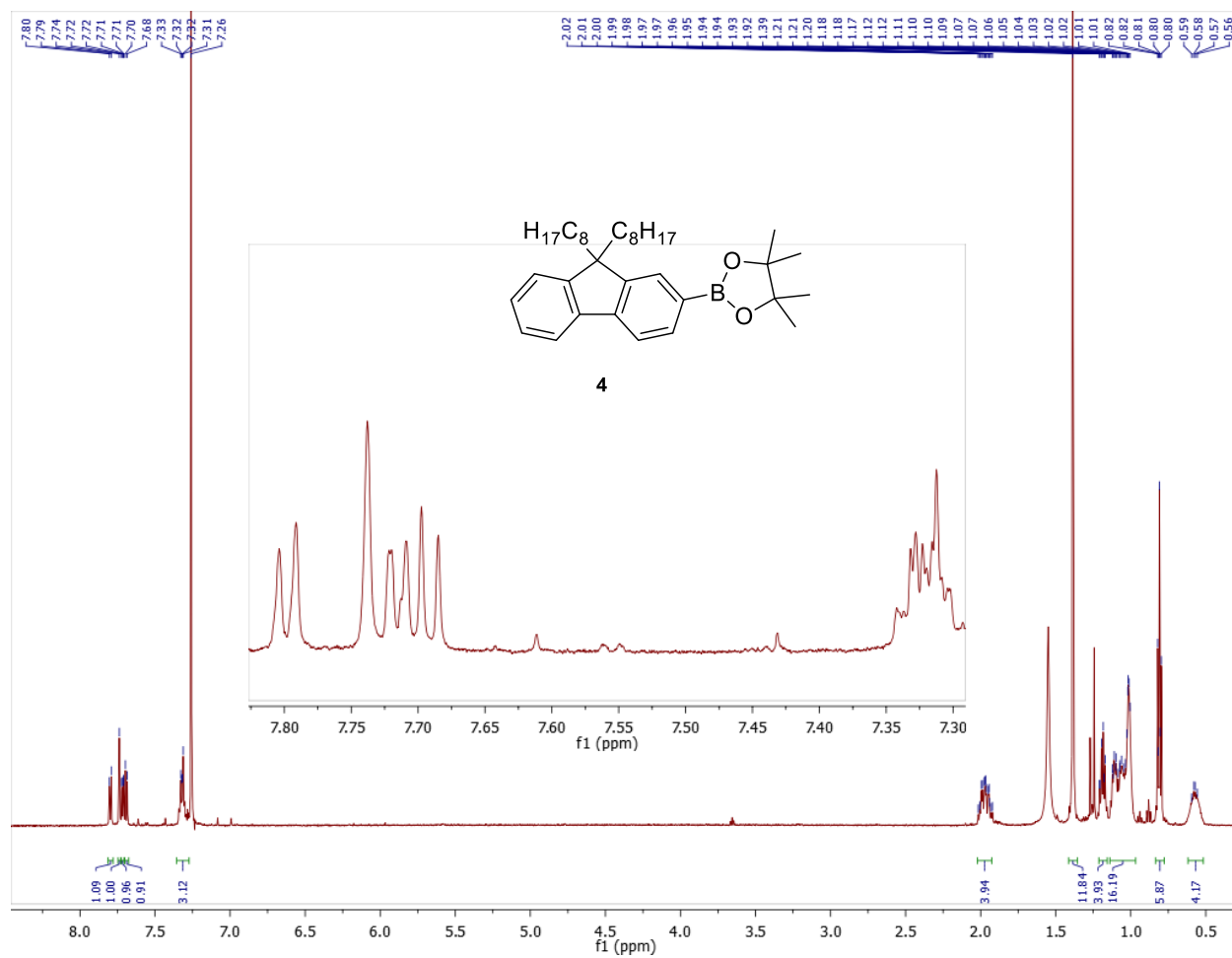
**Figure S6:  $^1\text{H}$  NMR Spectrum of 3**



**Figure S7: <sup>1</sup>H NMR Spectrum of S2**

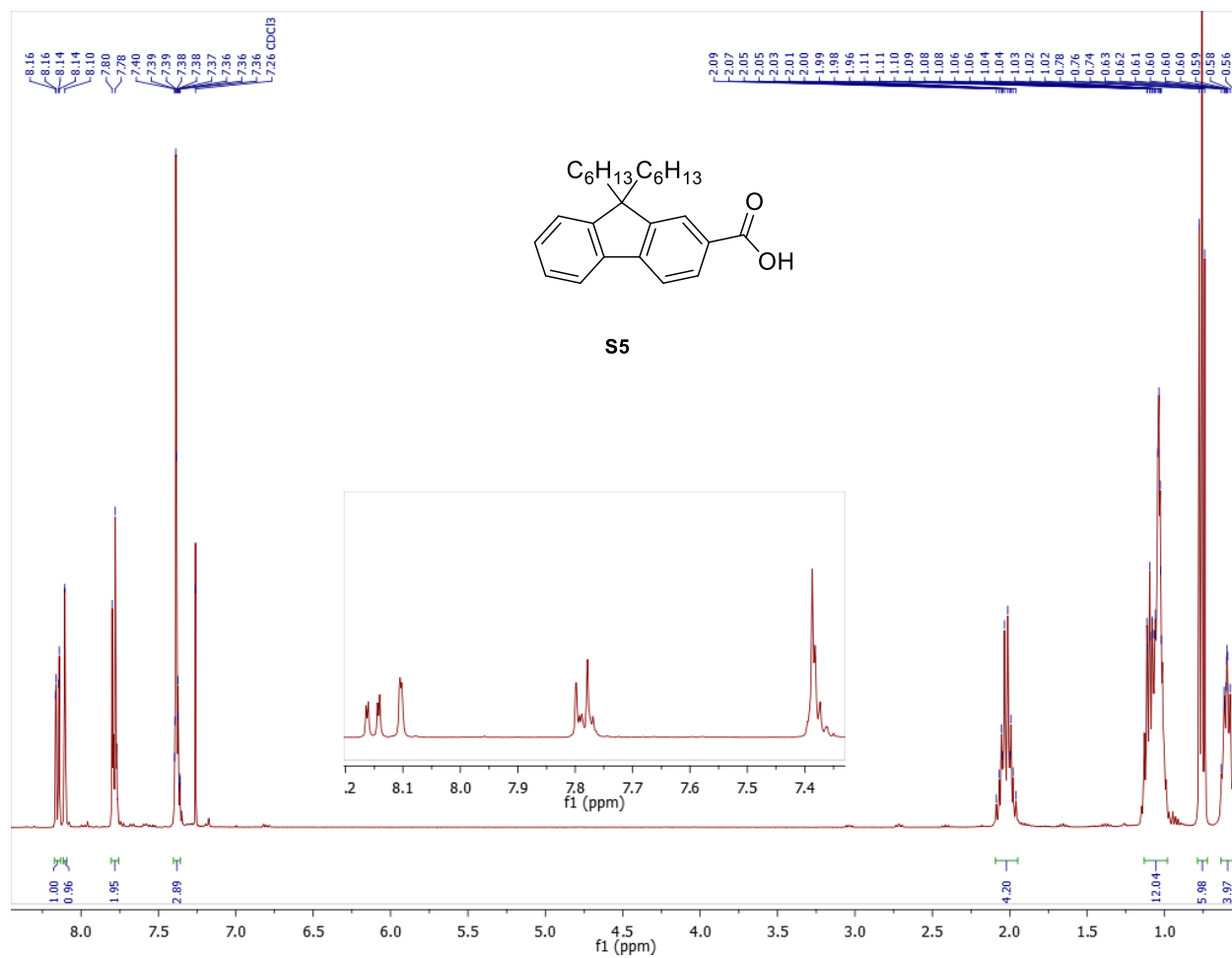


**Figure S8:  $^1\text{H}$  NMR Spectrum of S3**



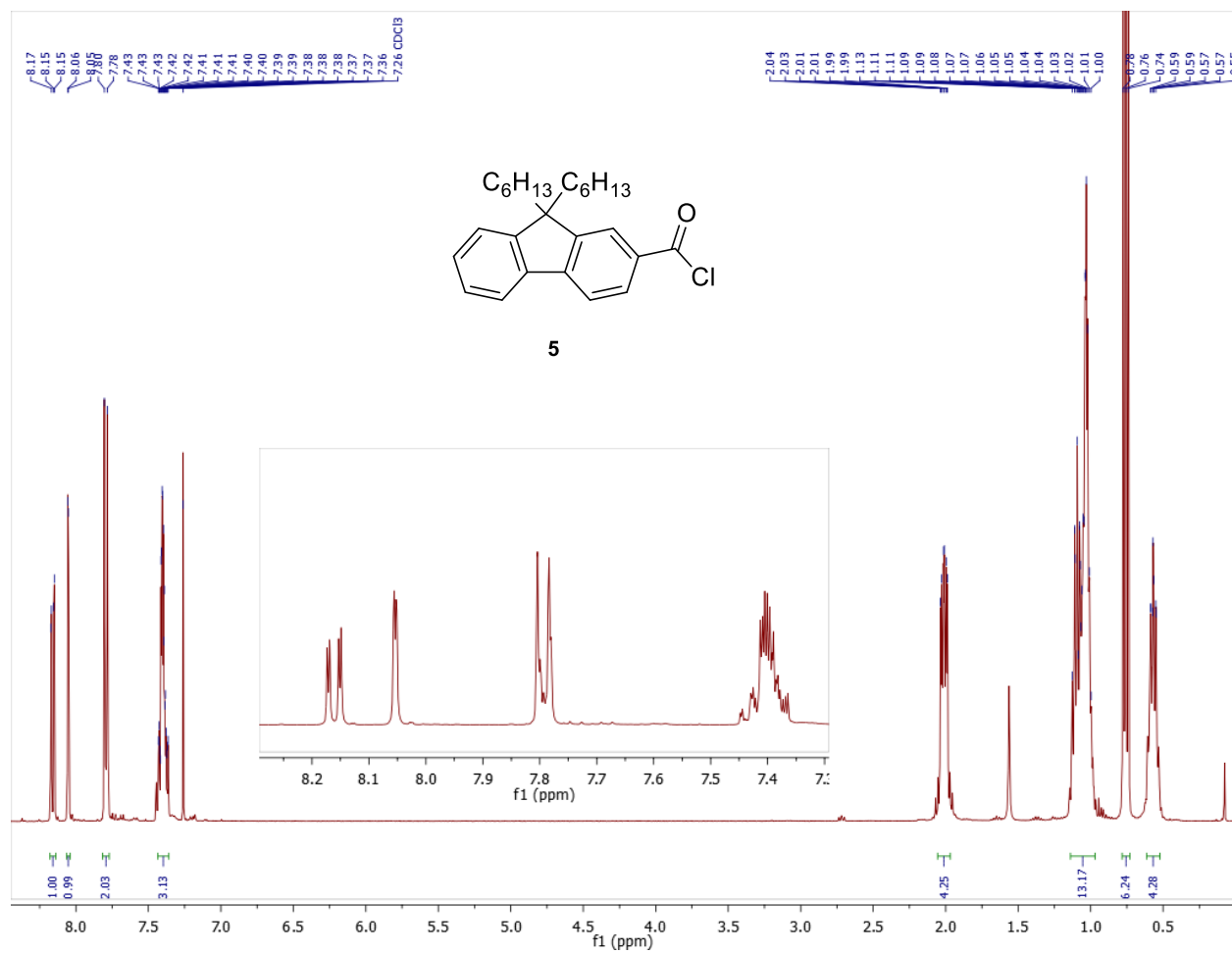
**Figure S9:  $^1\text{H}$  NMR Spectrum of **4****



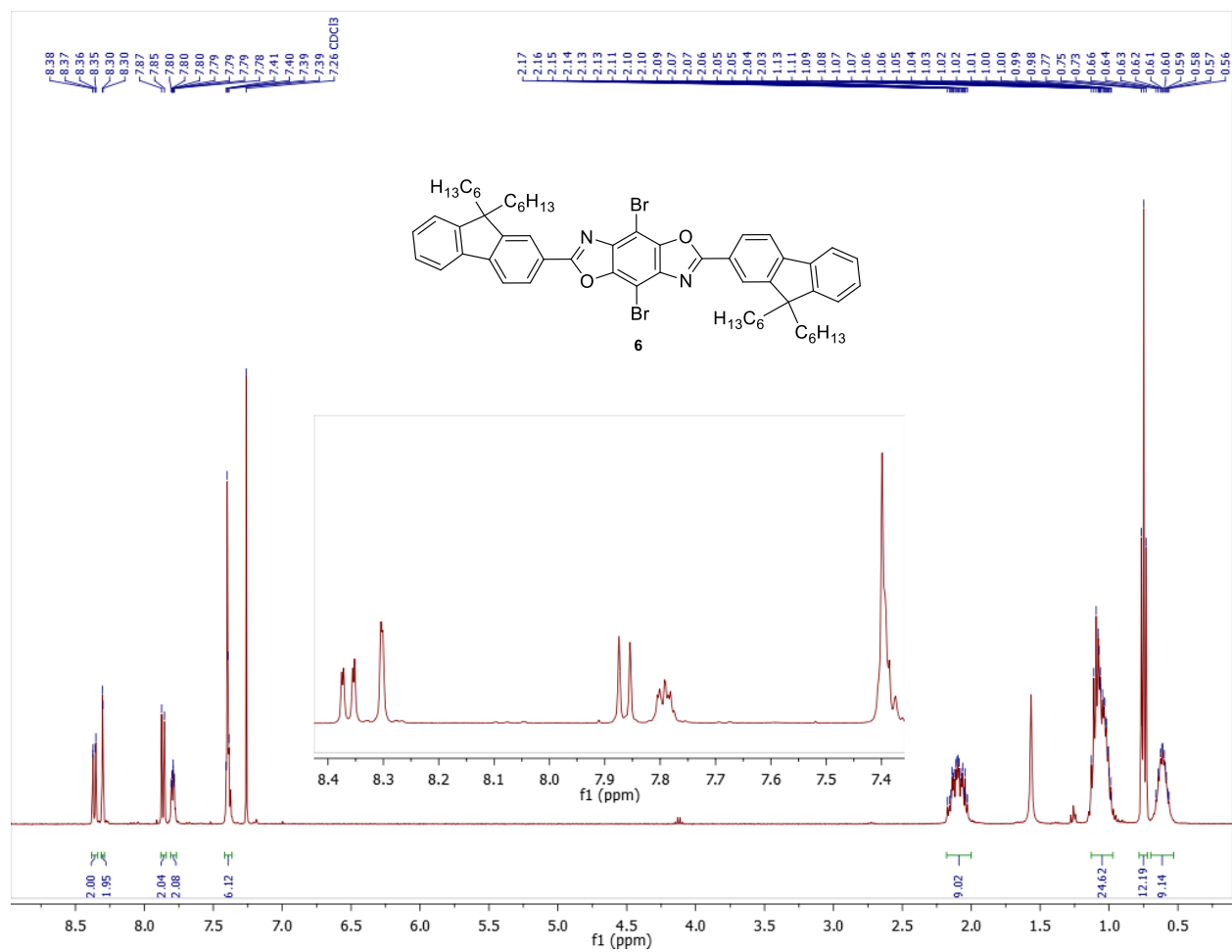


**Figure S11: <sup>1</sup>H NMR Spectrum of S5**

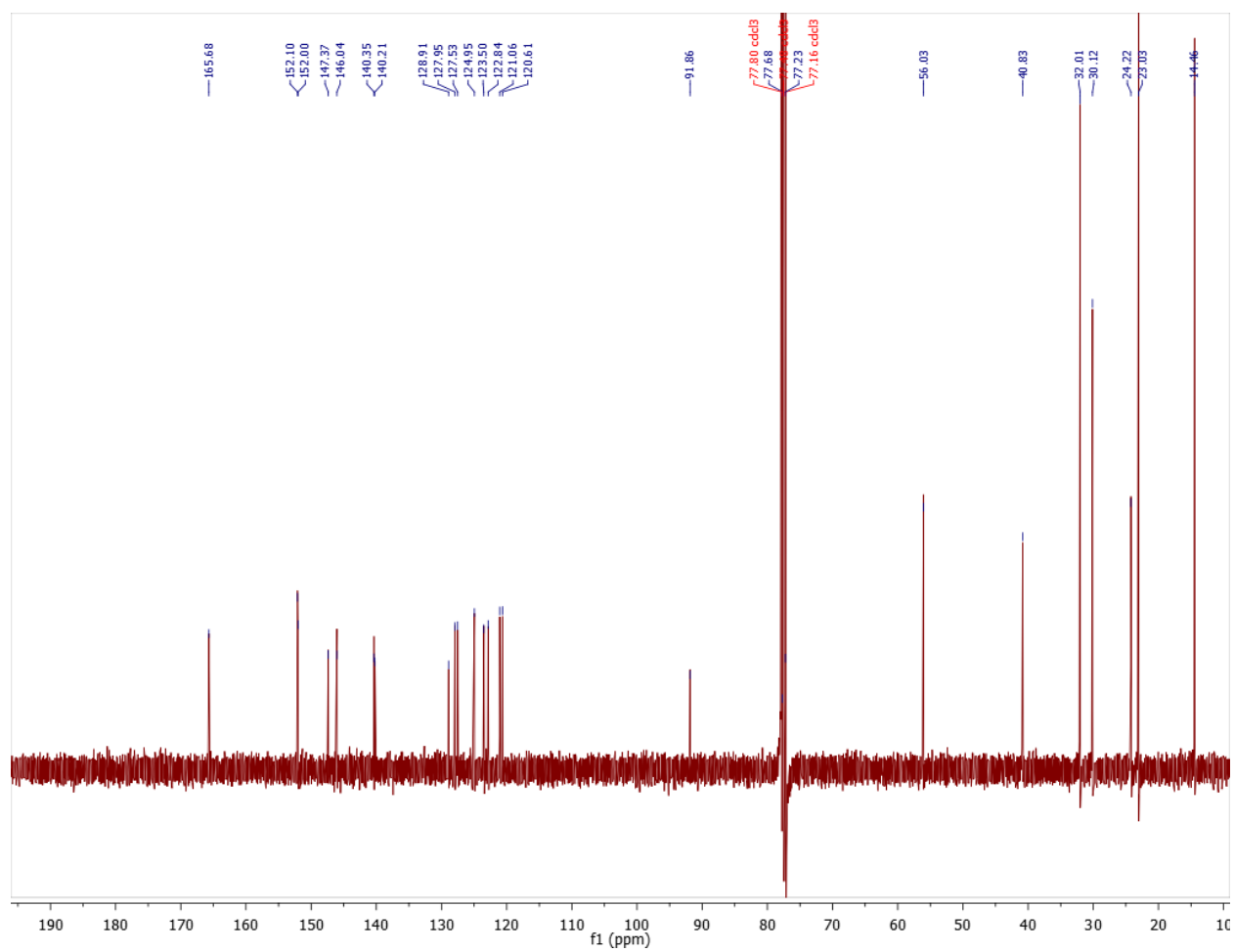




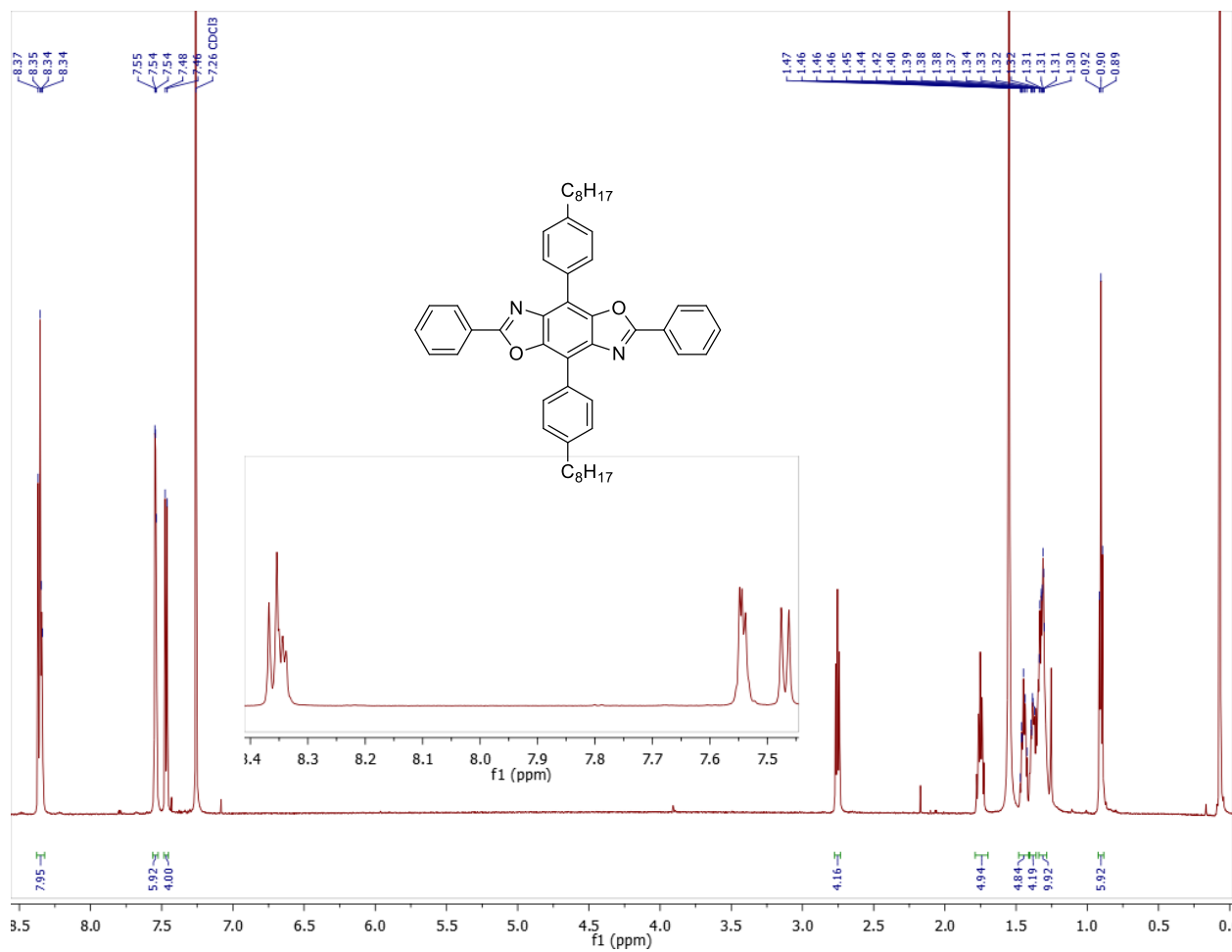
**Figure S12:  $^1\text{H}$  NMR Spectrum of **5****



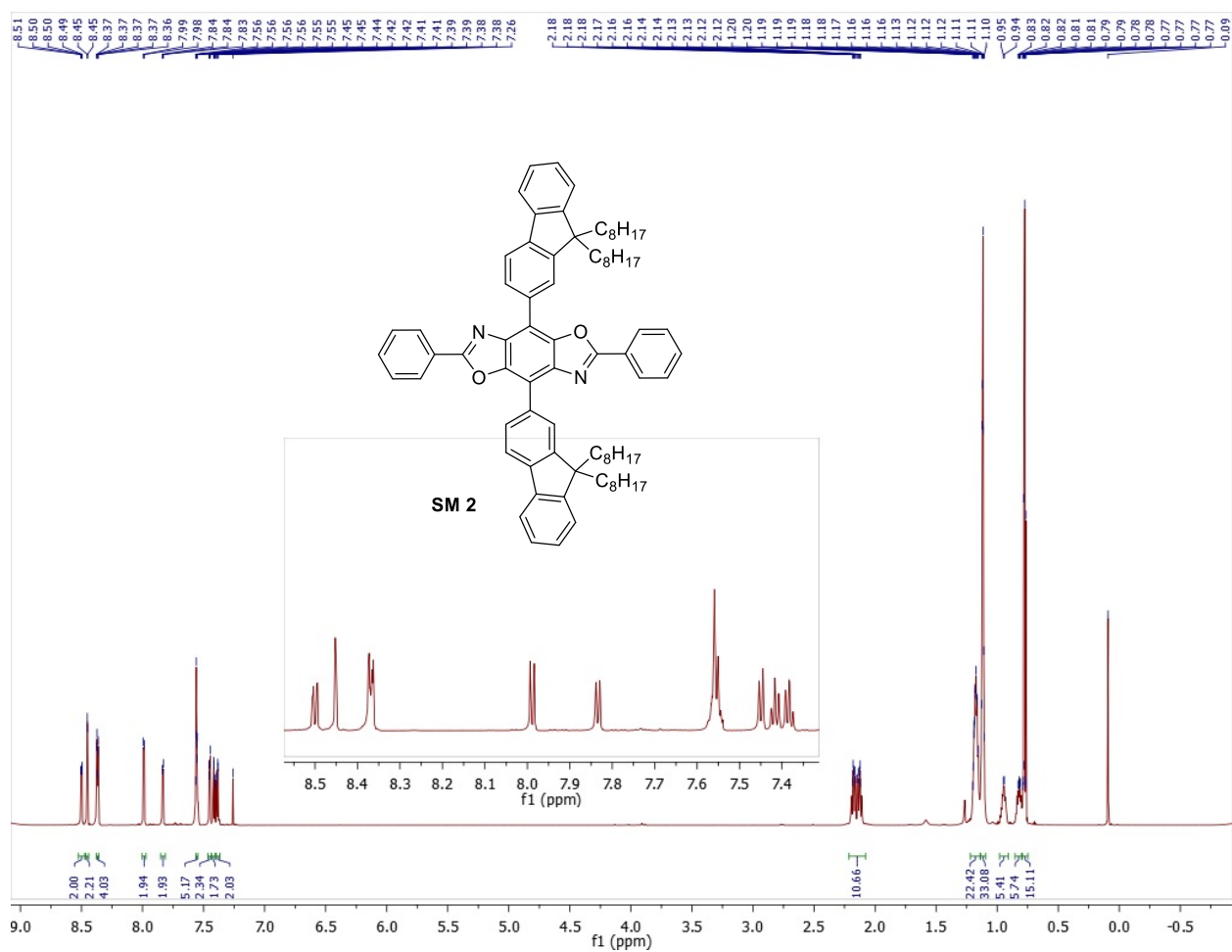
**Figure S13:  $^1\text{H}$  NMR Spectrum of **6****



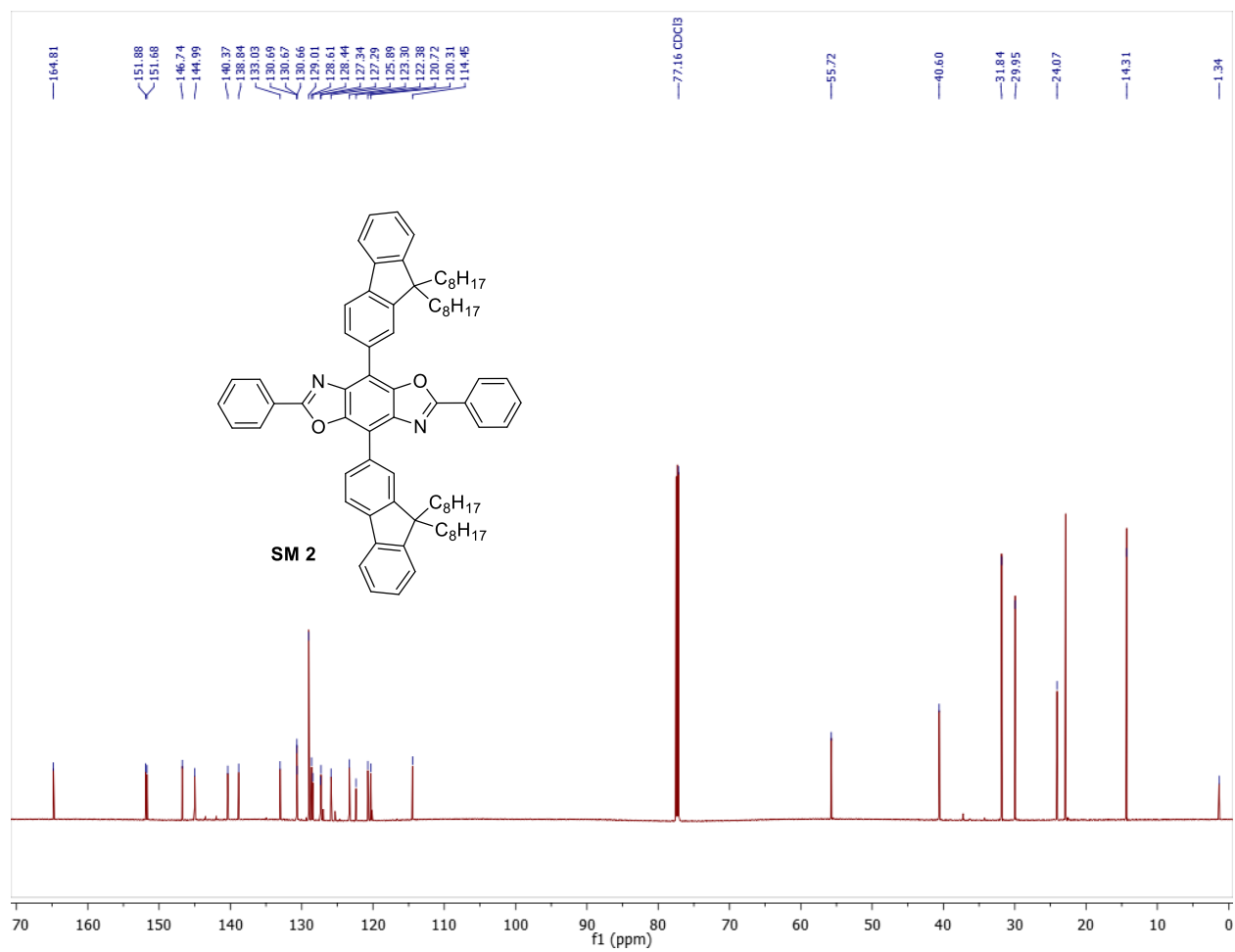
**Figure S14:** <sup>13</sup>C NMR Spectrum of **6**



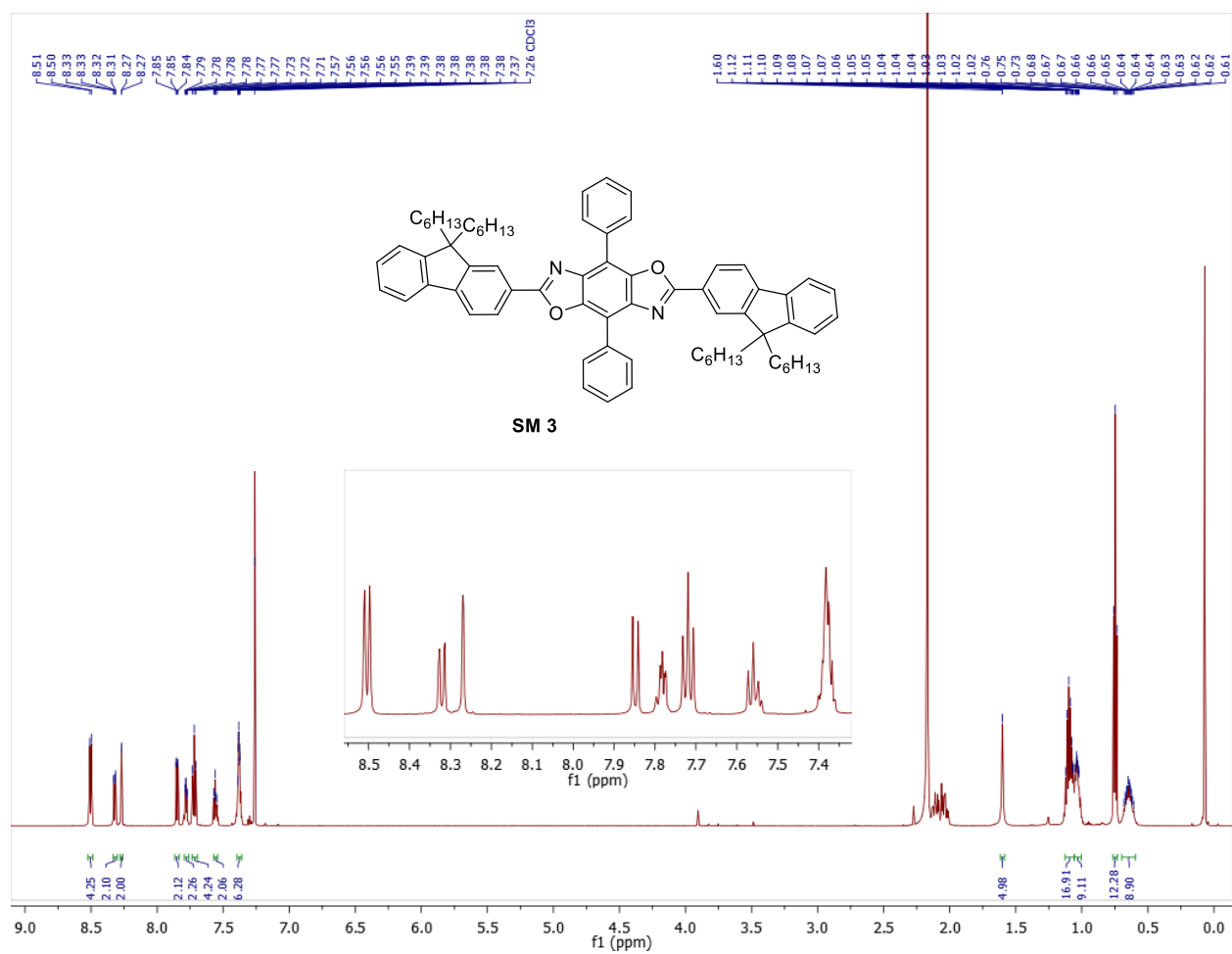
**Figure S15: <sup>1</sup>H NMR Spectrum of SM 1**



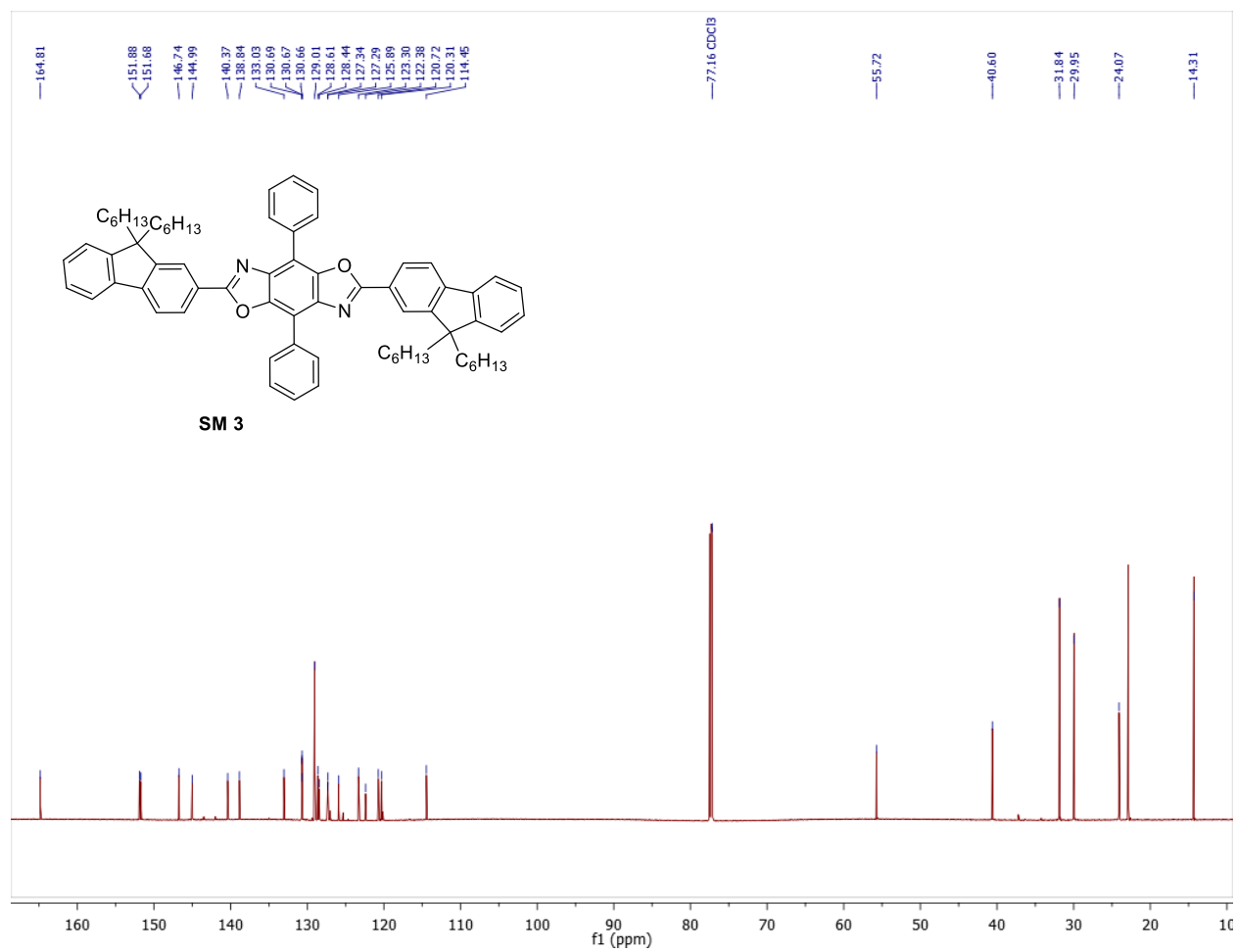
**Figure S16: <sup>1</sup>H NMR Spectrum of SM 2**



**Figure S17: <sup>13</sup>C NMR Spectrum of SM 2**

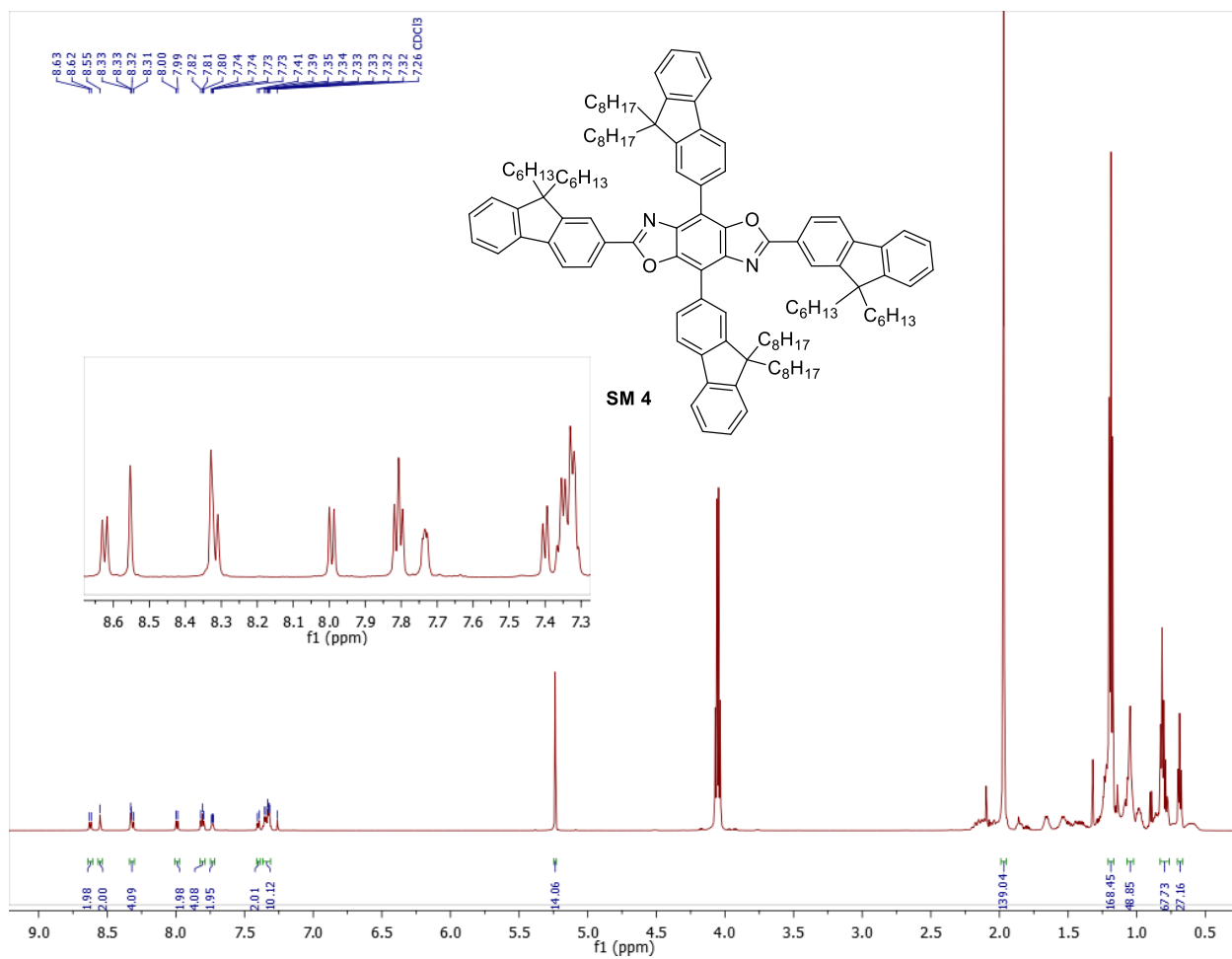


**Figure S18:  $^1\text{H}$  NMR Spectrum of SM 3**

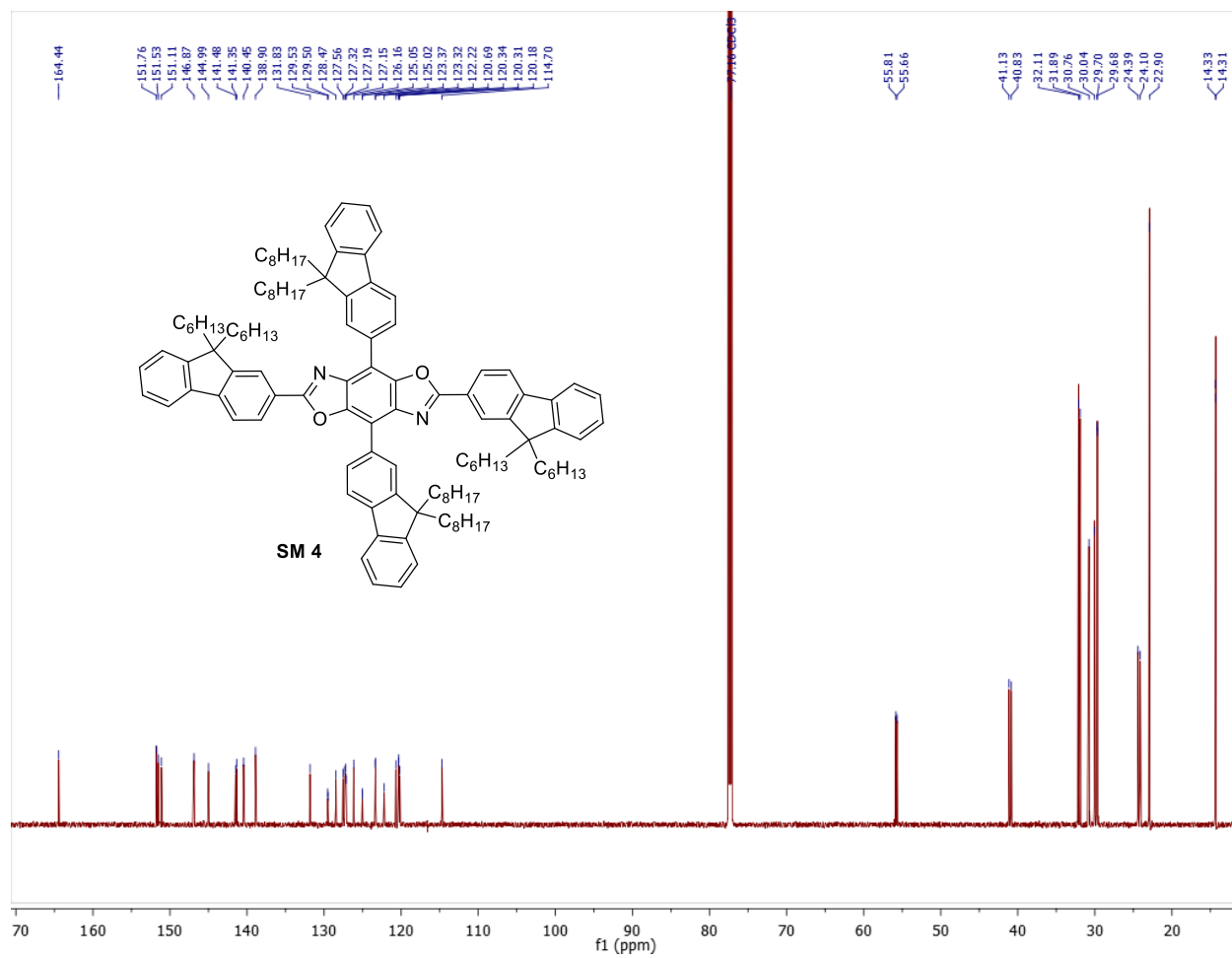


**Figure S19:** <sup>13</sup>C NMR Spectrum of SM 3





**Figure S20:  $^1H$  NMR Spectrum of SM 4**



**Figure S21: <sup>13</sup>C NMR Spectrum of SM 4**

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1. Ross, S. D.; Finkelstein, M.; Petersen, R. C., Solvent Effects in the Reactions of N-Bromosuccinimide with Toluene, Fluorene and Acenaphthene; Evidence for a Polar Mechanism in Propylene Carbonate. *Journal of the American Chemical Society* **1958**, *80* (16), 4327-4330.
2. (a) Rostami, A.; Guérin, G.; Taylor, M. S., Structure–Activity Relationships for Anion-Responsive Poly(squaramides): Support for an Analyte-Induced Noncovalent Polymer Cross-Linking Mechanism. *Macromolecules* **2013**, *46* (16), 6439-6450; (b) Xie, N.; Wang, J.; Guo, Z.; Chen, G.; Li, Q., Fluorene/Carbazole Alternating Copolymers Tethered with Polyhedral Oligomeric Silsesquioxanes: Synthesis, Characterization, and Electroluminescent Properties. *Macromolecular Chemistry and Physics* **2013**, *214* (15), 1710-1723.
3. Slota, J. E.; Elmalem, E.; Tu, G.; Watts, B.; Fang, J.; Oberhumer, P. M.; Friend, R. H.; Huck, W. T. S., Oligomeric Compatibilizers for Control of phase Separation in Conjugated Polymer Blend Films. *Macromolecules* **2012**, *45* (3), 1468-1475.